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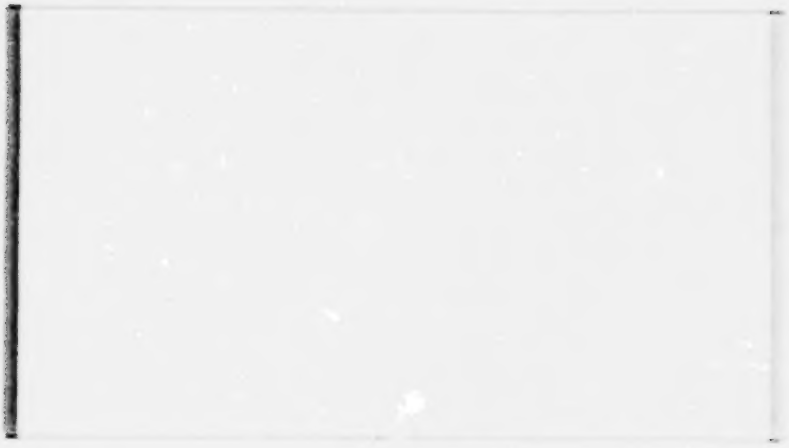

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# DISTRIBUTION OF 2,4-D AND PICLORAM RESIDUES IN ENVIRONMENTAL COMPONENTS ADJACENT TO A TREATED RIGHT-OF-WAY

Report No 87-49-K

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Biological Research Section
Chemical Research Department

## ABSTRACT

The objective of the study, as requested by Eastern Region, was to determine the presence of 2,4-D and picloram residues in a forest watershed adjacent to a Tordon 101 treated right-of-way located in Eastern Ontario. Residues of 2,4-D and picloram were detected in soil samples at least 36 M from the treated right-of-way 12 days, 2 and 8 months following herbicide application. Twenty-two months following herbicide application, the number of residue occurrences was greatly reduced (<4% of samples). Residues of both chemicals were also detected in water samples from a lake immediately adjacent to the treated right-of-way 12 days, 2 and 4 months after right-of-way treatment, however, these were well below the irrigation water quality criteria. 2,4-D and picloram residues were also detected in vegetation collected 1 M off the right-of-way. Whole body analysis of mice revealed a detectable level of picloram 12 days and 2 months following herbicide application.

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| 34-133-042 | 834.1 | March 6, 1987 | 87-49-K |

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## EXECUTIVE SUMMARY

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The objective of the study, as requested by Eastern Region, was to determine the presence of 2,4-D and picloram residues in a forest watershed adjacent to a Tordon 101 treated right-of-way located in Eastern Ontario. Attempts were made to explain any trends in distribution of either residue in terms of soil depth, slope, organic content, pH and soil particle size. Sampling for both residues in soil, vegetation, lake water sediment and representative fish and mammal species was conducted in areas adjacent to the right-of-way before herbicide treatment and at preselected times within a 22 month period following application. A systematic sampling design, 5x4 equally spaced intervals, was used to sample the terrestrial environment between the right-of-way and North Moonbeam Lake. Movement into the aquatic environment was determined by sampling a chain of four lakes whose watershed includes the right-of-way. Residues of both chemicals were detected in soil samples at least 36 m from the treated right-of-way 12 days, 2 and 8 months following herbicide application. No trends between residue distribution in the soil for either chemical and the physical/chemical characteristics of the sampling area were observed. Twenty-two months following herbicide application, the number of residue occurrences was greatly reduced (<4% of samples). Residues of both chemicals were also detected in water samples from a lake immediately adjacent to the treated right-of-way 12 days, 2 and 4 months after right-of-way treatment. These concentrations were, however, well below the irrigation water quality criteria. Both residues were also

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detected in vegetation collected 1 m off the right-of-way. Whole body analysis of mice revealed a detectable level of picloram 12 days and 2 months following herbicide application. Neither residue, however, was detected in fish flesh samples collected after treatment.

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To Dr. D.J. Mills
Manager Distribution Systems
Eastern Region

# DISTRIBUTION OF 2,4-D AND PICLORAM RESIDUES IN ENVIRONMENTAL COMPONENTS ADJACENT TO A TREATED RIGHT-OF-WAY

## INTRODUCTION

Selective herbicide application to non-compatible tree species is an integral part of vegetation management of Ontario Hydro rights-of-way. Tordon 101 is presently being used to control the growth of non-compatible woody plant species (ie. those which have the potential for interfering with power transmission) on rights-of-way in Northern and Eastern Ontario, whereas 2,4-D + 2,4-DP is generally used in Southern Ontario.

Tordon 101 consists of a mixture of triisopropanolamine salts of 2,4-D (2,4-dichlorophenoxyacetic acid) and picloram (4-amino 3,5,6-trichloropicolinic acid). The disappearance of these residues from soil on the right-of-way may be attributed to several processes: volatilization, photodecomposition, adsorption, leaching, runoff, and chemical and microbial decomposition (NRCC, 1974). The appearance of these residues at non targeted sites (soil, water, plants and animals) will be the result of leaching, runoff and perhaps volatilization.

Considerable research has been reported on herbicide movement from agricultural fields (see review - Wauchope 1978). Few studies however have investigated herbicide movement in a forested watershed. Differences in herbicide movement from forest watersheds and agricultural fields has been attributed to the higher organic matter content and the greater permeability of forest soils (Bouchard et al., 1985). Consequently, the volume of surface runoff from forest soils is reported to be less than from agricultural fields while the volume of water moving downward and laterally in the soil column will be greater.

Picloram is reversibly adsorbed on soil particles and is generally considered a mobile herbicide (Ghassemi et al., 1981) while 2,4-D is less mobile. The extent of adsorption and hence potential for mobility and leaching of both picloram and 2,4-D is dependent on soil type (primarily organic content), pH, application rate and precipitation events.

The objective of the present study, as requested by Eastern Region, was to determine the presence of 2,4-D and picloram residues in a forest watershed adjacent to an operationally treated right-of-way. Attempts were made to explain any trends in distribution of either residue in terms of soil depth, slope, organic content pH, and soil particle size. Samples were collected from the soil, vegetation and water bodies adjacent to the right-of-way as well as representative mammal and fish species.

## METHODS AND MATERIALS

The study was conducted at two sites along the Des Joachims power corridor located along the eastern boundary of Algonquin Park. These sites are located in the Murchison Township at the border of Airy Township and included a chain of four lakes whose watershed included part of the right-of-way (Figure 1). These areas were selected because of the site's proximity to the right-of-way and because of the presence of certain physiographical features which may be conducive to herbicide movement from the area of application. These included shallow soils and a steep slope between the right-of-way and water bodies at both the first study site (Crevice Lake) and the second site (North Moonbeam). In addition, the vegetation along this particular stretch of right-of-way was assessed as being among the densest of those available for study.

Sampling for 2,4-D and picloram residues in soil, vegetation lake water, sediment and representative fish and mammal species was conducted in areas adjacent to the right-of-way before herbicide treatment and at pre-selected times within a 22 month period following application. An exception was the collection of vegetation and soil samples from the Crevice site where sampling was limited to two months following herbicide application. The presence of herbicide in areas adjacent to North Moonbeam and Crevice Lakes was studied using a systematic sampling design from the right-of-way to each lake. A 5 transect X 4 equally spaced intervals sampling design was used to collect soil samples between North Moonbeam and the right-of-way. Samples from the Crevice Lake study site were collected at five equally spaced intervals along a single transect situated perpendicular to the right-of-way approximately 10 m from the lake.

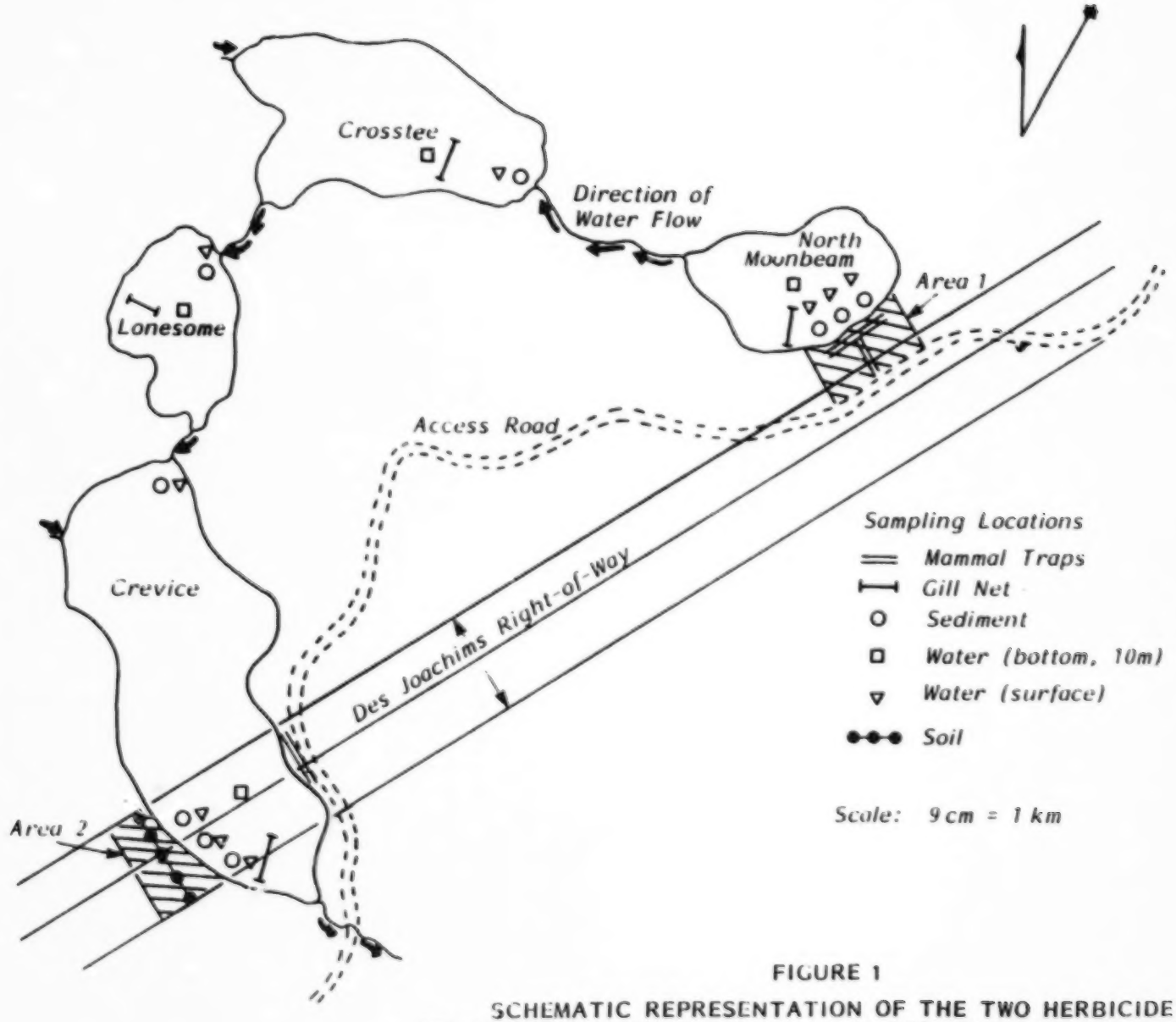


FIGURE 1

SCHEMATIC REPRESENTATION OF THE TWO HERBICIDE STUDY AREAS LOCATED ALONG THE DES JOACHIMS RIGHT-OF-WAY

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The North Moonbeam site was characterized in terms of vegetation density, soil depth and surface topography. The Crevice site was characterized only in terms of soil depth. Soil depth was determined by inserting a 2 m steel rod into the soil until bedrock was encountered. This parameter was determined at each soil sampling location as well as at 4 m intervals within the study area. Soil along transects 1,3 and 5 was further characterized by organic matter content and particle size. Organic matter content was determined by the amount of material lost on ignition at 550$^{o}$C for two hours and expressed as a percent of the total weight. Particle size was determined using the wet sieve method as described by Folk, 1968. Soil pH was measured for each of the top samples collected along transects 1,3 and 5 using a 1:1 soil/water ratio (v/v).

Surface topography of the North Moonbeam site as well as the adjacent section of right-of-way was determined using a transit. Contour lines were calculated at 4 m intervals and expressed as metres above the surface of North Moonbeam Lake.

Vegetation density, located on the right-of-way between towers 225 and 226, was determined by enumerating the number of live and dead stems eight months after herbicide application. The difference in percent survival (presence of a green cambium) of the target trees was used as a measure of effectiveness for the selective application of Tordon 101.

Precipitation (cm/m$^2$) was calculated from the amount of rainfall collected following herbicide application and prior to the initial sampling period using a customized rain gauge.

Presence of 2,4-D and picloram was determined in soil, vegetation, water, lake sediment, fish (flesh) and small mammal (whole body) samples collected at sites adjacent to the treated right-of-way. Sampling locations for all of the above are shown in Figures 1 and 4. Vegetation samples were collected from the forest within 1 m of the boundary between the forest and the right-of-way. Vegetation (herbaceous/woody composite) was collected at random from plants < 30 cm in height within a 0.25 m square plot at the beginning of each of the five transects.

Soil samples were collected using a 30 cm long by 2.0 cm diameter corer. The core sample was subsequently divided into three equal sections (top, middle and bottom).

Surface water samples (11) were collected along the 1 m depth contour of North Moonbeam and Crevice lakes and at the inflows of the remaining lakes. Bottom water samples were collected offshore at an approximate depth of 10 m using a Van Dorn

sampler. Lake sediments (0.5l) were sampled along the 1 m contour of North Moonbeam and Crevice Lakes as well as from just offshore of the inflow of each of the remaining lakes using a ponar grab.

Representative fish species (sport/coarse) were collected using gill nets consisting of 4 panels with mesh sizes increasing in 1.25 cm increments from 6.3 cm to 10 cm. Nets were set for a twenty-four hour period during each sampling time.

Small mammals were collected using museum snap traps along three trap lines set 5 m from the right-of-way edge towards North Moonbeam Lake, 5 m from the shore of North Moonbeam lake and along the shore of Crevice Lake right below the right-of-way. Fifteen traps were used on each line set 10 m apart.

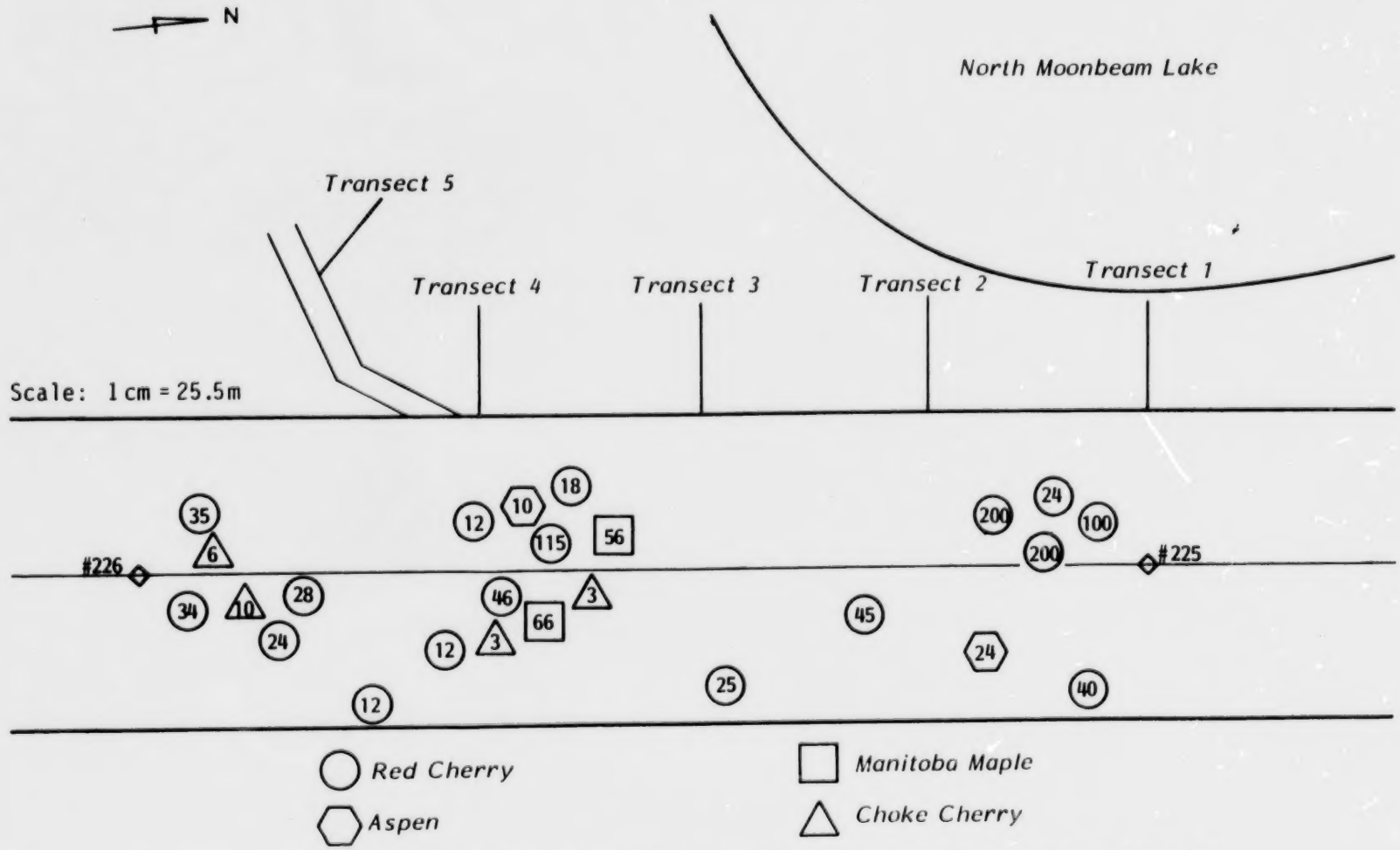
All samples were frozen (with the exception of the water samples) and returned to the laboratory for analysis. Residues of 2,4-D and picloram present in the samples were estimated quantitatively by gas-liquid chromatography (GLC). The herbicide content of the soil, vegetation, fish and small mammal samples was expressed as a function of the dry weight of the material extracted. The herbicide content of water and sediment samples was expressed on a weight to volume basis.

The percentage of 2,4-D and picloram recovered from samples using the above analytical procedure was 74 to 93% and 77 to 92% respectively for soil samples, 99% and 70 to 85% for water, 91% and 83% for sediment, 118% and 119% for vegetation, 91% and 85% for fish and 85% and 73% for mice samples. These recoveries were obtained from additional samples collected before herbicide application that were spiked with known amounts of the herbicide. Extraction and estimation procedures then followed. In several instances, 2,4-D and picloram residues were found in samples collected before herbicide application. These "apparent" herbicides have been encountered routinely in large scale pesticide extractions and determinations. The presence of "apparent" picloram in soil samples has been discussed in detail previously (Bjerke 1973).

## RESULTS

### Effectiveness of Herbicide Application

Red Cherry (*Prunus pensylvanica* L.), Manitoba Maple (*Acer negundo* L.), Poplar (*Populus tremuloides* Michx.) and Choke Cherry (*Prunus virginiana* L.) dominated the live woody vegetation community between the two towers on the right-of-way (Figure 2).




*Numbers in Symbols Indicate Approximate Abundance of Individual Trees at that Location*

FIGURE 2

DISTRIBUTION AND DENSITY OF THE DOMINANT TREE SPECIES LOCATED BETWEEN TOWERS 225 AND 226 ON THE DES JOACHIMS RIGHT OF WAY

166984 RD

The greatest cluster of trees was located on the western half of the right-of-way in the vicinity of Tower 225.

Red Cherry and Manitoba Maple represented 84% of the number of stems of the various species enumerated between Towers 225 and 226 (Table 1). Both species were successfully eliminated (>99%) by Tordon 101 when observations were made 8 months after herbicide application. The few Red Cherry that did survive (6) were in the center of clusters and appeared not to have been sprayed. Survivors of the other species did appear to have been sprayed but had sprouted deformed leaves. Red Oak was the only species that appeared to be tolerant to the application of Tordon 101. Red Oak tolerance of Tordon 101 was not unexpected and has been previously reported (Ontario Hydro Report No. 1041f29, 1984). The continued viability of a few individuals of Beech, Birch, Aspen and Balsam may be the result of inadequate spraying since their susceptibility to Tordon 101 has also been documented.

Table 1

Susceptibility of the various species to application of Tordon 101 eight months after herbicide application.

| Species | Number | % of Total | % Survival |
|---|---|---|---|
| Red cherry | 980 | 75 | <1% |
| M. Maple | 122 | 9 | 0 |
| Aspen | 52 | 4 | 9% |
| Choke cherry | 46 | 4 | 0 |
| Beech | 43 | 3.3 | 5% |
| Birch | 26 | 2.2 | 12% |
| Spruce | 15 | 1 | 0 |
| Willow | 10 | 0.7 | 0 |
| Balsam | 6 | 0.4 | 33% |
| Red Oak | 6 | 0.4 | 100% |
| Total | 1306 | 100% | |

## Physical Description of Study Sites

### Site 1 - Crevice Lake

Soil depth along the single transect at the first study site (Crevice Lake) was generally shallow and more variable than at the second study site - North Moonbeam (Figure 3). Mean soil depth across the right-of-way at this location was 30cm±12.

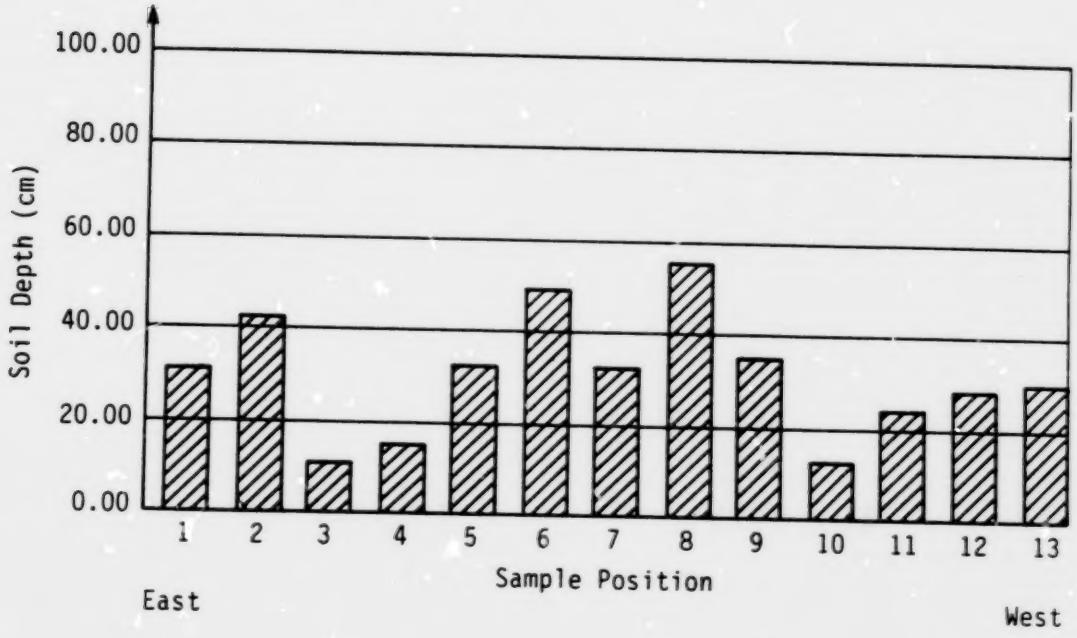



FIGURE 3

SOIL DEPTH ALONG A SAMPLING TRANSECT
POSITIONED PERPENDICULAR TO THE RIGHT-OF-WAY
AND SOUTH OF CREVICE LAKE
SAMPLE LOCATIONS WERE 1,4,7,10, AND 13

Table 2

Percent organic matter content and particle size (um) of soil samples collected at selected intervals along transects 1, 3 and 5 on the North Moonbeam site. T, M, B = Top, Middle, Bottom of the 30 cm core.

| | | % organic/particle size Transect | | |
|---|---|---|---|---|
| | | 1 | 3 | 5 |
| Right-of-way | T | 4.9 / .13 | 4.8 / .12 | 4.3 / .12 |
| | M | 3.0 / .12 | 3.5 / .13 | 3.8 / .14 |
| | B | 4.1 / .13 | 4.0 / .13 | 3.5 / .13 |
| A | T | 2.3 / .17 | 3.5 / .13 | 2.1 / .13 |
| | M | 0.9 / .12 | 3.5 / .13 | 1.2 / .13 |
| | B | 1.5 / .13 | 3.3 / .13 | 0.9 / .13 |
| B | T | 2.5 / .12 | 2.1 / .12 | 4.6 / .12 |
| | M | 1.1 / .13 | 2.1 / .13 | 1.2 / .13 |
| | B | 0.7 / .13 | 2.3 / .12 | 1.5 / .13 |
| C | T | 2.6 / .12 | 6.9 / .13 | 3.2 / .13 |
| | M | 4.9 / .12 | 1.7 / .12 | 3.0 / .13 |
| | B | 4.4 / .12 | 6.0 / .12 | 4.5 / .13 |
| D | T | 4.0 / .10 | 5.5 / .12 | 5.4 / .12 |
| | M | 4.9 / .12 | 7.6 / .12 | 5.4 / .12 |
| | B | 6.0 / .12 | 1.3 / .12 | 0.9 / .12 |

Site 2 - North Moonbeam Lake

Analysis of the surface topography between towers 225 and 226 at the second study site indicated that the access road represented the highest point on the right-of-way (Figure 4). Primarily, the area to the south of the road sloped west. Only about 25% of any potential runoff from the area between the two towers would have been directed towards North Moonbeam Lake.

The initial sampling period was scheduled to follow a significant storm event(s). Precipitation over the two weeks following herbicide application approximated 11.3 cm.

Topographical analysis of the sampling area between the right-of-way and North Moonbeam lake indicated that the slope was predominately north (Figure 4). Of the five transects sampled, transects 1 and 2 were the steepest followed by transects 3,5

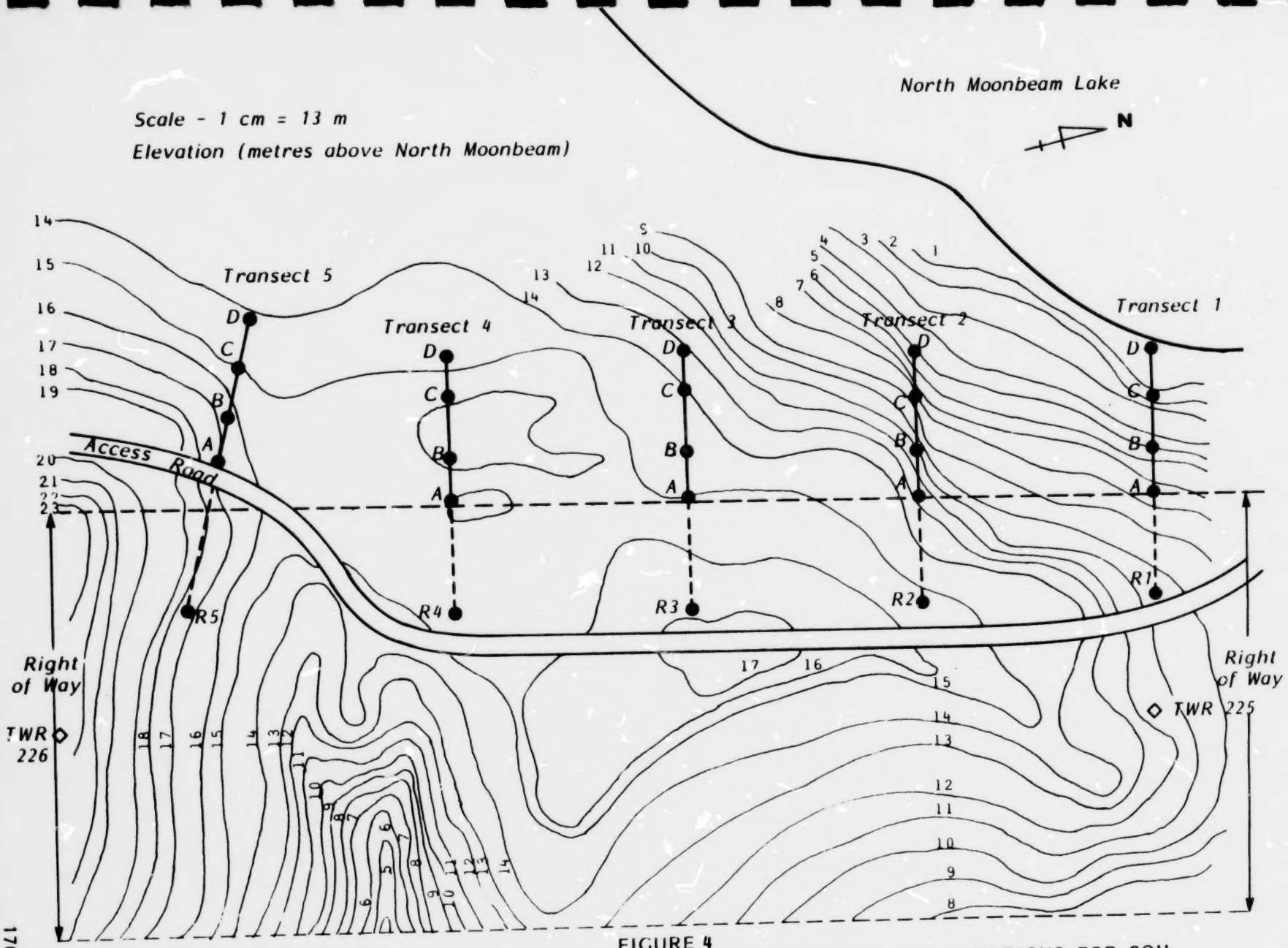



FIGURE 4
TOPOGRAPHY OF THE NORTH MOON STUDY SITE. OFF RIGHT-OF-WAY LOCATIONS FOR SOIL AND VEGETATION ALONG EACH TRANSECT ARE DENOTED AS A, B, C AND D. SOIL SAMPLING LOCATIONS ON THE RIGHT-OF WAY ARE LABELLED R1-R5

170097-RD

and 4. Soil depth among the five was generally similar with the exception of transect 1 where soil depth approaching the lake decreased dramatically (Figure 5).

Mean particle size was generally similar among all locations sampled between North Moonbeam Lake and the right-of-way (Table 1). Organic matter content (%) was less variable on the right-of-way than off the right-of-way. Organic matter content was generally higher on the right-of-way than off the right-of-way. The exceptions were locations situated within twelve meters of North Moonbeam Lake where values were comparable.

## Distribution of Herbicide Residues in Soil

### On the Right-of-Way

#### Site 1 - Crevice Lake

The presence of 2,4-D and picloram residues in soil samples collected before herbicide application at the Crevice study site can be attributed to the occurrence of apparent residues of either chemical during analytical procedure (see Materials and Method). Following herbicide application, both chemicals were found in a large number of samples and levels detected were substantially above the detection limit (Table 3). Levels of 2,4-D ranged from the detection limit to 2.38 ug/g, while picloram residues ranged from 0.02 to 0.48 ug/g. Values for both chemicals appeared to decrease with increasing soil depth. Herbicide residues were only detected in one sample of thirty collected two months after herbicide application.

#### Site 2 - North Moonbeam Lake

Neither 2,4-D nor picloram residues were detected in soil samples collected on the right-of-way adjacent to the North Moonbeam site before spraying (Table 4). Twelve days following herbicide application, 2,4-D residues ranged in concentration from 0.06 to 0.34 ug/g, while picloram residues ranged from a low of 0.03 to 3.15 ug/g. The characteristic ratio of 4:1 (w:w), 2,4-D to picloram in Tordon 101, was not evident. The highest values per soil core were found in transects 1 and 4 for both chemicals. No trend with depth for either of the chemicals was evident.

Two months following herbicide application the concentration of residues of both 2,4-D and picloram in soil samples on the right-of-way had decreased. This was particularly evident for picloram where previously high concentrations had decreased by a factor of ten. The two transects (1 and 4) where the highest

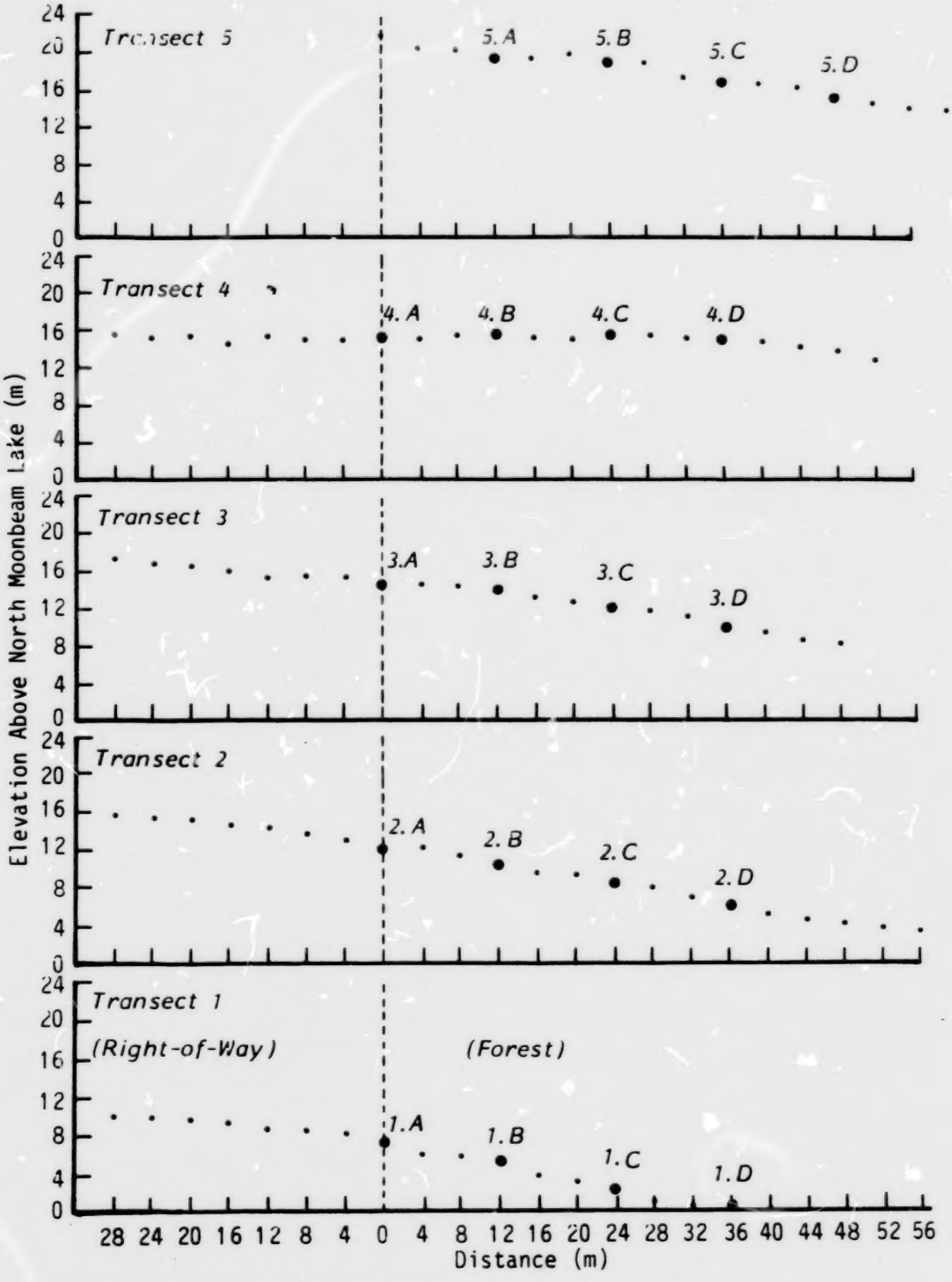



FIGURE 5

VERTICAL ELEVATION PROFILE FOR
THE NORTH MOONBEAM STUDY SITE

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TABLE 3

CONCENTRATION OF 2,4-D AND PICLORAM IN SOIL SAMPLES COLLECTED AT 5 POINTS ALONG A SINGLE TRANSECT LOCATED ON THE RIGHT-OF-WAY JUST SOUTH OF CREVICE LAKE; BEFORE, 12 DAYS AND 2 MONTHS AFTER TORDON 101 APPLICATION TO THE RIGHT-OF-WAY

BEFORE HERBICIDE APPLICATION (JULY, 1984)

| | 2,4-D (µg/g) | | | | | Picloram (µg/g) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 | 5 |
| TOP | 0.04 | 0.04 | 0.06 | 0.03 | * | * | * | 0.01 | 0.01 | * |
| MID | * | 0.06 | * | * | * | * | * | 0.03 | * | * |
| BOT | * | * | * | * | * | * | * | * | * | * |

12 DAYS AFTER HERBICIDE APPLICATION (AUG 1984)

| | 2,4-D (µg/g) | | | | | Picloram (µg/g) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 | 5 |
| TOP | 0.04 | 0.66 | 2.38 | 1.29 | 0.44 | * | 0.33 | 0.20 | 0.48 | 0.33 |
| MID | * | * | 0.99 | 0.09 | 0.04 | * | 0.02 | * | 0.03 | 0.02 |
| BOT | * | * | 0.08 | * | 0.02 | * | * | * | * | * |

2 MONTHS AFTER HERBICIDE APPLICATION (OCT 1984)

| | 2,4-D (µg/g) | | | | | Picloram (µg/g) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 | 5 |
| TOP | * | * | * | * | * | * | * | * | 0.01 | * |
| MID | * | * | * | * | * | * | * | * | * | * |
| BOT | * | * | * | * | * | * | * | * | * | * |

* - LIMITS OF DETECTION ARE <0.02 µg/g FOR 2,4-D
AND <0.01 µg/g FOR PIC

TABLE 4
CONCENTRATION OF THE HERBICIDES 2,4-D AND PICLORAM IN SOIL SAMPLES COLLECTED AT FOUR POINTS ALONG EACH OF FIVE TRANSECTS BETWEEN THE DES JOACHIMS RIGHT-OF-WAY AND NORTH MOONBEAM LAKE, BEFORE, 12 DAYS, 2 MONTHS AND 8 MONTHS AFTER TORDON 101 APPLICATION TO THE RIGHT-OF-WAY

| Application | Sample Point On Transect | Soil Core Subsample | Transect Number | 2,4-D Herbicide Concentration ( g/g) | | | | | Picloram Herbicide Concentration ( g/g) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 | 5 |
| Before Herbicide Application | Right-of-way | T | | - | - | - | - | - | - | - | - | - | - |
| | | M | | - | - | - | - | - | - | - | - | - | - |
| | | B | | - | - | - | - | - | - | - | - | - | - |
| | A | T | | - | - | - | - | - | - | - | - | - | 0.03 |
| | | M | | - | - | 0.05 | - | - | - | - | - | - | - |
| | | B | | - | - | - | - | - | - | - | - | - | - |
| | B | T | | - | - | - | - | - | - | - | - | - | - |
| | | M | | - | 0.07 | - | - | - | - | - | - | - | - |
| | | B | | - | - | - | - | - | - | - | - | - | - |
| | C | T | | - | - | - | - | - | - | - | - | - | - |
| | | M | | - | - | - | - | - | - | - | - | - | - |
| | | B | | - | - | - | - | - | - | - | - | - | - |
| | D | T | | - | - | - | - | - | - | - | - | - | - |
| | | M | | - | - | - | - | - | - | - | - | - | - |
| | | B | | - | - | - | - | - | - | - | - | - | - |
| 12 days After Herbicide Application | Right-of-way | T | | 0.09 | 0.06 | - | 0.28 | 0.06 | 3.15 | - | - | 0.72 | 0.13 |
| | | M | | 0.23 | - | - | 0.08 | - | 2.60 | - | - | 0.03 | - |
| | | B | | 0.34 | - | - | 0.12 | 0.07 | 0.48 | - | - | 0.13 | - |
| | A | T | | 0.06 | 0.04 | - | - | 0.03 | 0.04 | - | - | - | - |
| | | M | | - | - | - | - | - | - | - | - | - | - |
| | | B | | - | - | - | 0.04 | - | - | - | - | - | - |
| | B | T | | - | 0.08 | - | - | 0.05 | - | 0.04 | - | 0.06 | 0.09 |
| | | M | | - | - | 0.03 | 0.09 | - | - | 0.04 | - | 0.01 | - |
| | | B | | 0.04 | 0.02 | - | - | - | 0.01 | - | - | - | - |
| | C | T | | - | - | - | 0.05 | - | - | - | 0.02 | 0.02 | - |
| | | M | | - | - | - | - | - | - | - | - | - | - |
| | | B | | - | - | - | - | 0.08 | - | - | - | - | - |
| | D | T | | - | 0.02 | - | - | - | - | - | - | - | 0.01 |
| | | M | | 0.04 | - | - | - | - | - | - | - | - | - |
| | | B | | - | - | - | - | - | - | - | - | - | - |

**TABLE 4 (Cont'd)**

| Application | Sample Point On Transect | Soil Core Subsample | Transect Number | 2,4-D Herbicide Concentration (µg/g) | | | | | Picloram Herbicide Concentration (µg/g) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 | 5 |
| 2 months After Herbicide Application | Right-of-way | T | | - | 0.22 | 0.07 | - | 0.09 | - | 0.54 | 0.04 | 0.10 | - |
| | | M | | 0.03 | - | - | - | - | - | - | - | 0.02 | - |
| | | B | | 0.10 | 0.03 | - | - | - | 0.11 | 0.13 | - | 0.04 | - |
| | A | T | | - | 0.22 | - | - | - | - | 0.03 | - | - | - |
| | | M | | - | - | - | - | - | - | - | 0.01 | - | - |
| | | B | | - | - | - | 0.07 | - | - | - | - | - | - |
| | B | T | | - | 0.08 | 0.11 | - | - | 0.07 | - | - | - | - |
| | | M | | - | - | - | - | - | - | - | - | - | 0.02 |
| | | B | | - | 0.04 | - | - | - | - | - | - | - | - |
| | C | T | | 0.06 | - | - | - | - | - | 0.03 | - | - | - |
| | | M | | - | - | - | - | - | - | - | - | - | - |
| | | B | | - | - | - | - | - | - | - | - | - | - |
| | D | T | | - | - | - | - | - | - | - | - | 0.01 | - |
| | | M | | - | - | - | - | - | - | - | - | - | - |
| | | B | | - | - | - | - | - | - | - | - | - | - |
| 8 months After Herbicide Application | Right-of-way | T | | 0.02 | - | 0.02 | 0.14 | - | 0.03 | - | - | - | - |
| | | M | | - | - | 0.02 | 0.07 | 0.03 | - | - | 0.02 | - | - |
| | | B | | - | - | 0.03 | 0.42 | - | - | - | 0.02 | - | - |
| | A | T | | - | 0.03 | - | - | - | 0.02 | 0.01 | 0.01 | - | - |
| | | M | | - | 0.02 | - | 0.07 | - | 0.02 | 0.01 | 0.01 | - | - |
| | | B | | | 0.03 | - | - | - | - | - | - | - | - |
| | B | T | | - | 4.14 | - | - | - | - | - | - | - | - |
| | | M | | - | - | - | - | - | - | - | - | - | - |
| | | B | | - | - | - | 0.46 | - | - | - | - | - | - |
| | C | T | | 0.07 | - | - | - | - | 0.01 | - | - | - | - |
| | | M | | - | 0.29 | - | 0.35 | - | - | - | - | - | - |
| | | B | | - | - | 0.02 | - | - | - | 0.02 | 0.03 | - | - |
| | D | T | | 0.02 | - | - | - | - | - | - | 0.02 | - | 0.01 |
| | | M | | - | - | - | - | 0.04 | - | 0.02 | - | - | - |
| | | B | | - | - | - | - | 0.18 | 0.01 | 0.02 | - | - | - |

Key: T = Top of soil sample
M = Middle of soil sample
B = Bottom of soil Sample

*Limits of Detection: <0.02 for 2,4-D
<0.01 for Picloram

**TABLE 4 (Cont'd)**

| Application | Sample Point On Transect | Soil Core Subsample | Transect Number 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Herbicide Concentration (µg/g) | | | | | | | | | |
| | | | 2,4-D | | | | | Picloram | | | | |
| 22 months After Herbicide Application | Right-of-way | T | - | - | - | - | 0.08 | 0.04 | - | - | - | - |
| | | M | - | 0.07 | - | - | - | - | - | - | - | - |
| | | B | - | - | - | - | - | - | - | - | - | - |
| | A | T | 0.04 | - | - | - | - | - | 0.03 | - | - | - |
| | | M | - | - | - | - | - | - | - | - | - | - |
| | | B | - | - | - | - | - | - | - | - | - | - |
| | B | T | - | - | - | - | - | - | - | - | - | - |
| | | M | - | - | - | - | - | - | - | - | - | - |
| | | B | - | - | - | - | - | - | - | - | - | - |
| | C | T | 0.09 | - | - | - | - | - | - | - | - | - |
| | | M | - | - | - | - | - | - | - | - | - | - |
| | | B | - | - | 0.05 | - | - | - | - | - | - | - |
| | D | T | - | - | - | - | - | - | 1.10 | - | - | - |
| | | M | - | - | - | - | - | - | - | - | - | - |
| | | B | - | - | - | - | - | - | - | - | - | - |

Key: T = Top of soil sample
M = Middle of soil sample
B = Bottom of soil Sample

*Limits of Detection: <0.02 for 2,4-D
<0.01 for Picloram

concentrations for both chemicals were previously detected, reflected values comparable or less than neighbouring transects. Again, no trend with depth during this period was evident.

The concentration of both chemicals in soil samples collected on the right-of-way eight months following application showed that the concentration of both 2,4-D and picloram had further decreased. The number of occurrences of detectable levels of 2,4-D generally remained the same whereas for picloram it had decreased by half. Again no trend with depth was evident. Twenty-two months following treatment, detectable levels of either residue were still found but at fewer locations (Table 4).

Adjacent to the Right-of-Way

Generally, the presence of either chemical was not detected in soil samples collected adjacent to the right-of-way prior to herbicide application. The instances where the two chemicals were detected can be attributed to analytical procedure (see Materials and Method).

Residues of both 2,4-D and picloram were detected in soil samples collected 12 days after herbicide application from the five transects adjacent to the right-of-way. Values for both 2,4-D and picloram were however, considerably lower than those detected on the right-of-way. Concentrations for 2,4-D ranged from the detection limit of 0.02 to 0.09 ug/g. The range for picloram residues was also from the detection limit of 0.01 to 0.09 ug/g. No trend with depth for either chemical was apparent. The number of occurrences of either chemical decreased considerably with distance from the right-of-way. Both chemicals however, were detected at the limit of the study's experimental design (36 M from the right-of-way).

2,4-D and picloram residues were also detected in the soil adjacent to the treated right-of-way two months following treatment. The number of occurrences for either chemical however, decreased by about half in comparison to the 12 day samples. Again, no trend for either chemical with depth was evident.

Eight months following treatment, the presence of 2,4-D and picloram over the sampling area had increased compared to the previous sampling period. The greatest number of occurrences for either chemical was detected in the lower half of the sampling area or within 18 M of North Moonbeam Lake. The opposite was true for the previous sampling periods following herbicide application where the greatest occurrence was within the first 18 M from the right-of-way. Concentrations of 2,4-D and picloram were generally similar to previous sampling periods. An unusually

high value for 2,4-D was detected along Transect 2 approximately 9 M from the right-of-way.

Twenty-two months following treatment, the number of occurrences for either residue was greatly reduced (<4% of samples).

**Distribution of Herbicide Residues in Lakes Adjacent to the Right-of-Way**

Neither 2,4-D nor picloram residues were detected in the chain of four lakes, whose watershed included part of the right-of-way, before herbicide application (Table 5). Furthermore these residues were only found in one of the four lakes, Crevice Lake, twelve days after the right-of-way was treated. Levels in Crevice did not increase significantly within two months or in the case of 2,4-D, even four months later. Residue levels of picloram did however, increase by a factor of ten after four months. Residues of the two chemicals were not detected in any of the remaining lakes until four months later when both were found in North Moonbeam. Eight months following herbicide application, residues of the two chemicals could not be detected in any of the four lakes. Neither of the two residues were detected in bottom samples from any of the four lakes.

2,4-D residues in lake sediments were detected in North Moonbeam only (0.70 ug/g) twelve days after treatment of the right-of-way. Picloram residues were only found two months after herbicide application at the detection limit (0.01 ug/g) in samples from North Moonbeam and Crevice lakes.

**Distribution of Herbicide Residues in Biological Components Adjacent to the Right-of-Way**

Twelve days following herbicide application, the highest concentrations of 2,4-D and picloram in vegetation were detected at the top of transects 1 and 2 (Table 6). None of the leaves collected however exhibited any signs of contact damage similar to that observed on the treated right-of-way. The range of values for 2,4-D was similar two months following right-of-way treatment. The range for picloram however, decreased by a factor of ten between the two sampling periods. The concentrations of the two chemicals detected before herbicide application were close to the detection levels. The picloram values were attributable to apparent picloram (see Materials and Method).

Picloram residues in whole body mouse (*Microtus pennsylvanicus*) samples were not present prior to right-of-way treatment. Residues however, were detected 12 days and 2 months following

TABLE 5

CONCENTRATION OF THE HERBICIDES 2,4-D AND PICLORAM (μg/g DRY WT) IN VEGETATION COLLECTED ALONG THE BOUNDARY BETWEEN THE RIGHT-OF-WAY AND ADJACENT NORTH MOONBEAM STUDY SITE BEFORE, 12 DAYS AND 2 MONTHS AFTER APPLICATION OF TORDON 101 TO THE DES JOACHIMS RIGHT-OF-WAY

| Herbicide | Sampling Time/Sampling Position | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Before | | | | | +12 Days | | | | | +2 Months | | | | |
| | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 | 5 |
| 2,4-D | - | - | 0.7 | - | - | 1.9 | 3.4 | 0.8 | - | 0.6 | - | 2.9 | - | 0.9 | - |
| Picloram | - | 0.4 | - | - | 0.4 | 8.6 | 18.0 | 1.0 | - | - | - | 0.8 | - | 0.6 | - |

- detection level: 2,4-D <0.5, picloram <0.3

TABLE 6

CONCENTRATION OF THE HERBICIDES 2,4-D AND PICLORAM IN WATER SAMPLES (SURFACE) FROM FOUR LAKES; BEFORE, 12 DAYS, 2 MONTHS, 4 MONTHS AND 8 MONTHS AFTER APPLICATION OF TORDON 101 TO THE DES JOACHIMS RIGHT OF WAY
VALUES ARE EXPRESSED AS A MEAN (n=3) + ONE STANDARD DEVIATION

| Lake | Herbicide | Sampling Time | | | | | |
|---|---|---|---|---|---|---|---|
| | | Before | +12 days | +2 months | +4 months | +8 months | +22 months |
| | | Herbicide concentration (µg/L) | | | | | |
| North Moonbeam | 2,4-D | - | - | - | 0.06±0.01 | - | - |
| | Picloram | - | - | - | 0.07±0.03 | - | - |
| Crosstee | 2,4-D | - | - | - | + | - | - |
| | Picloram | - | - | - | + | - | - |
| Lonesome | 2,4-D | - | - | - | + | - | - |
| | Picloram | - | 0.03* | - | + | - | - |
| Crevice | 2,4-D | - | 0.06±0.01 | 0.06±0.02 | 0.08±0.01 | - | - |
| | Picloram | - | 0.04±0.01 | 0.07±0.08 | 0.28±0.08 | - | - |

- = not detected
+ = no sample collected

detection limits: 2,4-D = <0.05 µg/L
Picloram = <0.03 µg/L

* = only one sample

herbicide application (0.03 and 0.01 ug/g respectively). Analyses of whole body mouse samples, collected before and after herbicide application, for 2,4-D residues gave inconsistent results, with residues being found before and after herbicide application.

Analyses of fish flesh samples for 2,4-D residues gave inconsistent results, with residues being found before and after herbicide application. Picloram was not detected in fish flesh (White Sucker; Catastomus commersoni) in any of the lakes (North Moonbeam or Crevice) immediately adjacent to the right-of-way before or after herbicide application

DISCUSSION

Results indicated that the greatest occurrences of 2,4-D and picloram residues at non-targeted sites followed several precipitation events that totaled above the thirty year average rainfall of 8.79 cm for the month of August (Algonquin Park station, 45 35'N 78 33'W; Canadian Climate Normals, Ontario 1980) and following snowmelt. Movement and dissipation of 2,4-D and picloram in soil have been found to be negligible under low soil moisture conditions in other field studies (Grover et al. 1985, Hunter and Stobbe 1972 and Norris et al.1982). Herbicide loss from a treated area following snowmelt has been equated to losses following a severe rainfall (Nicholaichuk and Grover 1983). Suffling et al (1974) however have shown that losses of picloram and 2,4-D from a Tordon 101 sprayed podsol in a Great Lakes forest clearcut can also be negligible even after several runoff events.

The importance of clay, organic matter content and soil pH for the retention of 2,4-D and picloram in soil has been reported (Grover 1973, Grover 1968, Keys and Friesen 1968, respectively). The high organic matter content and low pH characteristics of the soil sampled during our study should have favoured adsorption. The variability in detection of either 2,4-D or picloram among the sampling locations during the course of the study suggests that soil adsorption was minimal. The underlying layer of sandy soil detected at all locations may have minimized the importance of the above characteristics by enhancing the mobility of both residues.

The persistence of picloram is reported to be greater than 2,4-D, 4.5 months-4.6 years as opposed to 7-54 days (Ou 1984, Norris et al 1982 and NRCC 1974, Neary et al 1985, respectively) with the

difference attributable primarily due to the reduced susceptibility of picloram to microbial degradation. Our results indicated no apparent difference in the persistence of the two residues during the study.

Both 2,4-D and picloram have been reported to be absorbed by plants primarily via roots or leaves (Bukovac 1976). Residues of 2,4-D and picloram in the vegetation, located just inside the forest in our study, probably originated from the soil since the leaves of the plants collected did not exhibit any contact damage.

Results indicated that residue levels in mice were approximately 0.03 ug/g-bw (body weight). These levels were considerably lower than the LD50 reported for rats (8000 mg/kg-bw, NRCC 1974). Furthermore, studies have indicated that picloram is rapidly eliminated in the urine following ingestion and does not appear to accumulate to any significant extent in body tissues (Leasure and Getzandaner 1964 and Kutschinski and Riley 1969).

The concentrations of either residue found in any of the lakes were below the water quality objectives set by the Ministry of the Environment for irrigation water (MOE 1983). The earlier occurrence of 2,4-D and picloram residues in Crevice Lake (12 days) compared to North Moonbeam Lake (4 months) may have been attributable to the shallowness of the soil and the slope of the land between the right-of-way and the lake. In contrast, run-off from the right-of-way to North Moonbeam Lake would have been impeded by a greater soil depth, vegetation and a reduced slope.

The increase of picloram with time in Crevice Lake may have simply reflected an additive effect by run-off from the right-of-way following successive precipitation events. Detectable residue of 2,4-D has been found to persist for 3-4 weeks in some aquatic ecosystems and upwards of four months in others (Frank and Comes 1967, Wojtalik et al. 1971 and Schultz and Harman 1974). In our study, residues persisted for the four months following herbicide application and were not detected after the winter months. Disappearance of the residues was probably due to dilution, degradation or removal downstream. Transfer of water downstream or among the chain of four lakes however, would have been hindered by beaver activity in each of the four lakes studied. Loss to the sediment during our study appeared to be minimal for both residues. Although information regarding the partitioning of picloram between the water and sediment in a lake is lacking it is probable that because this residue exhibits a low affinity for soil (NRCC 1974) then an equal low affinity would be exhibited towards sediment. 2,4-D on the other hand has

been shown to be adsorbed to sediment components. The breakdown of 2,4-D has been shown to be dependent upon the nutrient status of the river and not the availability of organisms capable of degrading the herbicide (Nesbitt and Watson 1980). Furthermore, degradation of 2,4-D in water has been reported to be several orders of magnitude slower as compared to degradation rates in the sediment (DeLaune and Salinas 1985).

The 96-h LC50 for Rainbow Trout has been reported to be 19.3 mg/L for picloram acid (Mayes and Dill 1984). The levels of picloram detected in the lakes during our study were at least an order of magnitude less than the above value. The influence of 2,4-D has been shown to be even less toxic (Sergeant et al 1971).

## CONCLUSIONS

1) Red Cherry and Manitoba Maple represented 84% of the number of live stems of the various species enumerated between Towers 225 and 226. Both species were eliminated (>99%) by the application of Tordon 101.

2) Residues of Tordon 101 were detected in the soil adjacent to the treated right-of-way during each of the sampling periods (12 days, 2, 8 and 22 months after herbicide application). 2,4-D and picloram residues were generally observed to move at least 36 M from the right-of-way. Trends with depth and organic content were not apparent. The underlying layer of sand may have enhanced the mobility of both residues.

3) Both residues were detected in vegetation (herbaceous/woody composite) collected 1 M off the right-of-way 12 days and 2 months after herbicide application. Evidence of contact damage was not evident on any of the leaves.

4) Analyses of whole body mouse samples indicated picloram concentrations of 0.03 and 0.01 ug/g 12 days and 2 months following herbicide application, respectively. Evidence of contact damage was not evident on any of the leaves.

5) Both residues were detected in Crevice Lake 12 days, 2 and 4 months following herbicide application but not following snowmelt. 2,4-D and picloram were detected in North Moonbeam Lake only 4 months after right-of-way treatment. These levels were below the water quality criterion set for these residues by MOE for irrigation water.

6) Picloram was not detected in fish flesh (white sucker) in any of the lakes immediately adjacent to the treated right-of-way.

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